

UNITED STATES PATENT APPLICATION FOR:

FORMATION OF A TANTALUM-NITRIDE LAYER

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FORMATION OF A TANTALUM-NITRIDE LAYER

BACKGROUND OF THE DISCLOSURE

5 **Field of the Invention**

The present invention relates to formation of one or more barrier layers and, more particularly to one or more barrier layers formed using chemisorption techniques.

Description of the Background Art

10 In manufacturing integrated circuits, one or more barrier layers are often used to inhibit diffusion of one or more materials in metal layers, as well as other impurities from intermediate dielectric layers, into elements underlying such barrier layers, such as transistor gates, capacitor dielectrics, transistor wells, transistor channels, electrical barrier regions, interconnects, among other known elements of integrated circuits.

15 Though a barrier layer may limit to prevent migration of unwanted materials into such elements, its introduction creates an interface at least in part between itself and one or more metal layers. For sub half-micron ($0.5\ \mu\text{m}$) semiconductor devices, microscopic reaction at an interface between metal and barrier layers can cause degradation of integrated circuits, including but not limited to increased electrical resistance of such
20 metal layers. Accordingly, though barrier layers have become a component for improving reliability of interconnect metallization schemes, it is desirable to mitigate "side effects" caused by introduction of such barrier layers.

Compounds of refractory metals such as, for example, nitrides, borides, and carbides are targets as diffusion barriers because of their chemical inertness and low
25 resistivities (e.g., sheet resistivities typically less than about $200\ \mu\Omega\text{-cm}$). In particular, borides such as, including but not limited to titanium diboride (TiB_2), have been used as a barrier material owing to their low sheet resistivities (e. g., resistivities less than about $150\ \mu\Omega\text{-cm}$).

Boride barrier layers are conventionally formed using chemical vapor deposition
30 (CVD) techniques. For example, titanium tetrachloride (TiCl_4) may be reacted with diborane (B_2H_6) to form titanium diboride (TiB_2) using CVD. However, when Cl-based chemistries are used to form boride barrier layers, reliability problems can occur. In

particular, boride layers formed using CVD chlorine-based chemistries typically have a relatively high chlorine (Cl) content, namely, chlorine content greater than about 3 %. A high chlorine content is undesirable because migrating chlorine from a boride barrier layer into adjacent interconnection layer may increase contact resistance of such interconnection layer and potentially change one or more characteristics of integrated circuits made therewith.

Therefore, a need exists for barrier layers for integrated circuit fabrication with little to no side effects owing to their introduction. Particularly desirable would be a barrier layer useful for interconnect structures.

SUMMARY OF THE INVENTION

An aspect of the present invention is film deposition for integrated circuit fabrication. More particularly, at least one element from a first precursor and at least one element from a second precursor is chemisorbed on a surface. The at least one element from the first precursor and the at least one element from the second precursor are chemisorbed to provide a tantalum-nitride film. This sequence may be repeated to increase tantalum-nitride layer thickness. This type of deposition process is sometimes called atomic layer deposition (ALD). Such a tantalum-nitride layer may be used as a barrier layer.

Another aspect is forming the tantalum-nitride layer using in part annealing of at least one tantalum-nitride sublayer. This annealing may be done with a plasma.

Another aspect is using a plasma source gas as a nitrogen precursor. The plasma source gas may be used to provide a plasma, which may be sequentially reacted or co-reacted with a tantalum containing precursor.

These and other aspects of the present invention will be more apparent from the following description.

BRIEF DESCRIPTION OF THE DRAWINGS

The teachings of the present invention can be readily understood by considering the following detailed description in conjunction with the accompanying drawings, in which:

FIGS. 1 and 4 depict schematic illustrations of exemplary portions of process systems in accordance with one or more integrated circuit fabrication aspects of the present invention;

FIGs. 2a-2c depict cross-sectional views of a substrate structure at different stages of integrated circuit fabrication;

FIGs. 3a-3c depict cross-sectional views of a substrate at different stages of chemisorption to form a barrier layer; and

FIG. 5 depicts a cross-sectional view of a substrate structure at different stages of integrated circuit fabrication incorporating one or more tantalum-nitride barrier sublayers post plasma anneal.

DETAILED DESCRIPTION

FIG. 1 depicts a schematic illustration of a wafer processing system 10 that can be used to form one or more tantalum-nitride barrier layers in accordance with aspects of the present invention described herein. System 10 comprises process chamber 100, gas panel 130, control unit 110, along with other hardware components such as power supply 106 and vacuum pump 102. For purposes of clarity, salient features of process chamber 100 are briefly described below.

Process Chamber

Process chamber 100 generally houses a support pedestal 150, which is used to support a substrate such as a semiconductor wafer 190 within process chamber 100. Depending on process requirements, semiconductor wafer 190 can be heated to some desired temperature or within some desired temperature range prior to layer formation using heater 170.

In chamber 100, wafer support pedestal 150 is heated by an embedded heating element 170. For example, pedestal 150 may be resistively heated by applying an electric current from an AC power supply 106 to heating element 170. Wafer 190 is, in turn, heated by pedestal 150, and may be maintained within a desired process temperature range of, for example, about 20⁰C to about 500⁰C.

Temperature sensor 172, such as a thermocouple, may be embedded in wafer support pedestal 150 to monitor the pedestal temperature of 150 in a conventional manner.

For example, measured temperature may be used in a feedback loop to control electric current applied to heating element 170 from power supply 106, such that wafer temperature can be maintained or controlled at a desired temperature or within a desired temperature range suitable for a process application. Pedestal 150 may optionally be heated using radiant heat (not shown).

Vacuum pump 102 is used to evacuate process gases from process chamber 100 and to help maintain a desired pressure or desired pressure within a pressure range inside chamber 100. Orifice 120 through a wall of chamber 100 is used to introduce process gases into process chamber 100. Sizing of orifice 120 conventionally depends on the size of process chamber 100.

Orifice 120 is coupled to gas panel 130 in part by valve 125. Gas panel 130 is configured to receive and then provide a resultant process gas from two or more gas sources 135, 136 to process chamber 100 through orifice 120 and valve 125. Gas sources 135, 136 may store precursors in a liquid phase at room temperature, which are later heated when in gas panel 130 to convert them to a vapor-gas phase for introduction into chamber 100. Gas panel 130 is further configured to receive and then provide a purge gas from purge gas source 138 to process chamber 100 through orifice 120 and valve 125.

Control unit 110, such as a programmed personal computer, work station computer, and the like, is configured to control flow of various process gases through gas panel 130 as well as valve 125 during different stages of a wafer process sequence. Illustratively, control unit 110 comprises central processing unit (CPU) 112, support circuitry 114, and memory 116 containing associated control software 113. In addition to control of process gases through gas panel 130, control unit 110 may be configured to be responsible for automated control of other activities used in wafer processing - such as wafer transport, temperature control, chamber evacuation, among other activities, some of which are described elsewhere herein.

Control unit 110 may be one of any form of general purpose computer processor that can be used in an industrial setting for controlling various chambers and sub-processors. CPU 112 may use any suitable memory 116, such as random access memory, read only memory, floppy disk drive, hard disk, or any other form of digital storage, local or remote. Various support circuits may be coupled to CPU 112 for supporting system 10. Software routines 113 as required may be stored in memory 116 or executed by a second

computer processor that is remotely located (not shown). Bi-directional communications between control unit 110 and various other components of wafer processing system 10 are handled through numerous signal cables collectively referred to as signal buses 118, some of which are illustrated in FIG. 1.

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Barrier Layer Formation

FIGs. 2a-2c illustrate exemplary embodiment portions of tantalum-nitride layer formation for integrated circuit fabrication of an interconnect structure in accordance with one or more aspects of the present invention. For purposes of clarity, substrate 200 refers to any workpiece upon which film processing is performed, and substrate structure 250 is used to denote substrate 200 as well as other material layers formed on substrate 200. Depending on processing stage, substrate 200 may be a silicon semiconductor wafer, or other material layer, which has been formed on wafer 190 (shown in FIG. 1).

FIG. 2a, for example, shows a cross-sectional view of a substrate structure 250, having a dielectric layer 202 thereon. Dielectric layer 202 may be an oxide, a silicon oxide, carbon-silicon-oxide, a fluoro-silicon, a porous dielectric, or other suitable dielectric formed and patterned to provide contact hole or via 202H extending to an exposed surface portion 202T of substrate 200. More particularly, it will be understood by those with skill in the art that the present invention may be used in a dual damascene process flow.

FIG. 2b illustratively shows tantalum-nitride layer 204 formed on substrate structure 250. Tantalum-nitride layer 204 is formed by chemisorbing monolayers of a tantalum containing compound and a nitrogen containing compound on substrate structure 250.

Referring to FIG. 2c, after the formation of tantalum-nitride layer 204, a portion of layer 204 may be removed by etching in a well-known manner to expose a portion 202C of substrate 200. Portion 202C may be part of a transistor gate stack, a capacitor plate, a node, a conductor, or like conductive element. Next, contact layer 206 may be formed thereon, for example, to form an interconnect structure. Contact layer 206 may be selected from a group of aluminum (Al), copper (Cu), tungsten (W), and combinations thereof.

Contact layer 206 may be formed, for example, using chemical vapor deposition (CVD), physical vapor deposition (PVD), electroplating, or a combination thereof. For example, an aluminum (Al) layer may be deposited from a reaction of a gas mixture containing dimethyl aluminum hydride (DMAH) and hydrogen (H₂) or argon (Ar) or other DMAH containing mixtures, a CVD copper layer may be deposited from a gas mixture containing Cu⁺²(hfac)₂ (copper hexafluoro acetylacetonate), Cu⁺²(fod)₂ (copper heptafluoro dimethyl octanediene), Cu⁺¹hfac TMVS (copper hexafluoro acetylacetonate trimethylvinylsilane), or combinations thereof, and a CVD tungsten layer may be deposited from a gas mixture containing tungsten hexafluoride (WF₆). A PVD layer is deposited from a copper target, an aluminum target, or a tungsten target.

Moreover, layer 206 may be a refractory metal compound including but not limited to titanium (Ti), tungsten (W), tantalum (Ta), zirconium (Zr), hafnium (Hf), molybdenum (Mo), niobium (Nb), vanadium (V), and chromium (Cr), among others. Conventionally, a refractory metal is combined with reactive species, such as for example chlorine (Cl) or fluorine (F), and is provided with another gas to form a refractory metal compound. For example, titanium tetrachloride (TiCl₄), tungsten hexafluoride (WF₆), tantalum pentachloride (TaCl₅), zirconium tetrachloride (ZrCl₄), hafnium tetrachloride (HfCl₄), molybdenum pentachloride (MoCl₅), niobium pentachloride (NbCl₅), vanadium pentachloride (VCl₅), or chromium tetrachloride (CrCl₄) may be used as a refractory metal-containing compound gas.

Though layer 206 is shown as formed on layer 204, it should be understood that layer 204 may be used in combination with one or more other barrier layers formed by CVD or PVD. Accordingly, layer 204 need not be in direct contact with layer 206, but an intervening layer may exist between layer 206 and layer 204.

Monolayers are chemisorbed by sequentially providing a tantalum containing compound and a nitrogen containing compound to a process chamber. Monolayers of a tantalum containing compound and a nitrogen containing compound are alternately chemisorbed on a substrate 300 as illustratively shown in FIGs. 3a-3c.

FIG. 3a depicts a cross-sectional view of an exemplary portion of substrate 300 in a stage of integrated circuit fabrication, and more particularly at a stage of barrier layer formation. Tantalum layer 305 is formed by chemisorbing a tantalum-containing compound on surface portion 300T of substrate 300 by introducing a pulse of a tantalum

containing gas 135 (shown in FIG. 1) into process chamber 100 (shown in FIG. 1). Tantalum containing gas 135 (shown in FIG. 1) may be a tantalum based organo-metallic precursor or a derivative thereof. Examples of such precursors include but are not limited to pentaethylmethylamino-tantalum (PEMAT; $\text{Ta}[\text{N}(\text{C}_2\text{H}_5\text{CH}_3)_2]_4$), pentadiethylamino-
5 tantalum (PDEAT), pentadimethylamino-tantalum (PDMAT), and any and all of derivatives of PEMAT, PDEAT, or PDMAT. Other tantalum containing precursors include without limitation $\text{Ta}(\text{NMe}_2)_5$, $\text{Ta}(\text{NEt}_2)_5$, TBTDET ($\text{Ta}(\text{NEt}_2)_3$ or $\text{C}_{16}\text{H}_{39}\text{N}_4\text{Ta}$), tantalum halides for example TaX_5 where X is fluorine (F), bromine (Br) or chlorine (Cl), and derivatives thereof.

10 Wafer 190 is maintained approximately below a thermal decomposition temperature of a selected tantalum precursor or a derivative thereof to be used and maintained at a pressure of approximately less than 100 Torr. Additionally, wafer 190 may be heated by heating element 170. An exemplary temperature range for precursors identified herein is approximately 20 to 400 degrees Celsius ($^{\circ}\text{C}$). For example,
15 approximately 150 to 300 $^{\circ}\text{C}$ may be used for PEMAT.

Though temperatures below a thermal decomposition temperature may be used, it should be understood that other temperatures, namely those above a thermal decomposition temperature, may be used. An example temperature ranges above a thermal decomposition temperature is approximately 400 to 600 $^{\circ}\text{C}$. Accordingly, some
20 thermal decomposition may occur; however, the main, more than 50 percent, deposition activity is by chemisorption. More generally, wafer surface temperature needs to be high enough to induce significant chemisorption of precursors instead of physisorption, but low enough to prevent significant decomposition of precursors. If the amount of decomposition during each precursor deposition is significantly less than a layer, then the
25 primary growth mode will be ALD. Accordingly, such a film will tend to have ALD properties. However, it is possible if a precursor significantly decomposes, but an intermediate reactant is obtained preventing further precursor decomposition after a layer of intermediate reactant is deposited, then an ALD growth mode may still be obtained.

While not wishing to be bound by theory, it is believed that this tantalum-
30 containing precursor combines tantalum atoms with one or more reactive species. During tantalum layer 305 formation, these reactive species form byproducts that are transported from process chamber 100 by vacuum system 102 while leaving tantalum deposited on

surface portion 300T. However, composition and structure of precursors on a surface during atomic-layer deposition (ALD) is not precisely known. A precursor may be in an intermediate state when on a surface of wafer 190. For example, each layer may contain more than simply elements of tantalum (Ta) or nitrogen (N); rather, the existence of more complex molecules having carbon (C), hydrogen (H), and/or oxygen (O) is probable. Additionally, a surface may saturate after exposure to a precursor forming a layer having more or less than a monolayer of either tantalum (Ta) or nitrogen (N). This composition or structure will depend on available free energy on a surface of wafer 190, as well as atoms or molecules involved. Once all available sites are occupied by tantalum atoms, further chemisorption of tantalum is blocked, and thus the reaction is self-limiting.

After layer 305 of a tantalum containing compound is chemisorbed onto substrate 300, excess tantalum containing compound is removed from process chamber 10 by vacuum system 102 (shown in FIG. 1). Additionally, a pulse of purge gas 138 (shown in FIG. 1) may be supplied to process chamber 10 to facilitate removal of excess tantalum containing compound. Examples of suitable purge gases include but are not limited to helium (He), nitrogen (N₂), argon (Ar), and hydrogen (H₂), among others, and combinations thereof that may be used.

With continuing reference to FIGS. 3a-c and renewed reference to FIG. 1, after process chamber 100 has been purged, a pulse of ammonia gas (NH₃) 136 is introduced into process chamber 100. Process chamber 100 and wafer 190 may be maintained at approximately the same temperature and pressure range as used for formation of layer 305.

In FIG. 3b, a layer 307 of nitrogen is illustratively shown as chemisorbed on tantalum layer 305 at least in part in response to introduction of ammonia gas 136. While not wishing to be bound by theory, it is believed that nitrogen layer 307 is formed in a similar self-limiting manner as was tantalum layer 305. Each tantalum layer 305 and nitrogen layer 307 in any combination and in direct contact with one another form a sublayer 309, whether or not either or both or neither is a monolayer. Though ammonia gas is used, other N containing precursors gases may be used including but not limited to N_xH_y for x and y integers (e.g., N₂H₄), N₂ plasma source, NH₂N(CH₃)₂, among others.

After an ammonia gas compound is chemisorbed onto tantalum layer 305 on substrate 300 to form nitrogen monolayer 307, excess ammonia gas compound is removed

from process chamber 10 by vacuum system 102, and additionally, a pulse of purge gas 138 may be supplied to process chamber 10 to facilitate this removal.

Thereafter, as shown in FIG. 3c, tantalum and nitrogen layer deposition in an alternating sequence may be repeated with interspersed purges until a desired layer 204 thickness is achieved. Tantalum-nitride layer 204 may, for example, have a thickness in a range of approximately 0.0002 microns (2 Å) to about 0.05 microns (500 Å), though a thickness of approximately 0.001 microns (10 Å) to about 0.005 microns (50 Å) may be a sufficient barrier. Moreover, a tantalum-nitride layer 204 may be used as a thin film insulator or dielectric, or may be used as a protective layer for example to prevent corrosion owing to layer 204 being relatively inert or non-reactive. Advantageously, layer 204 may be used to coat any of a variety of geometries.

In FIGs. 3a-3c, tantalum-nitride layer 204 formation is depicted as starting with chemisorption of a tantalum containing compound on substrate 300 followed by chemisorption of a nitrogen containing compound. Alternatively, chemisorption may begin with a layer of a nitrogen containing compound on substrate 300 followed by a layer of a tantalum containing compound.

Pulse time for each pulse of a tantalum containing compound, a nitrogen containing compound, and a purge gas is variable and depends on volume capacity of a deposition chamber 100 employed as well as vacuum system 102 coupled thereto. Similarly, time between each pulse is also variable and depends on volume capacity of process chamber 100 as well as vacuum system 102 coupled thereto. However, in general, wafer 190 surface must be saturated by the end of a pulse time, where pulse time is defined as time a surface is exposed to a precursor. There is some variability here, for example (1) a lower chamber pressure of a precursor will require a longer pulse time; (2) a lower precursor gas flow rate will require a longer time for chamber pressure to rise and stabilize requiring a longer pulse time; and (3) a large-volume chamber will take longer to fill, longer for chamber pressure to stabilize thus requiring a longer pulse time. In general, precursor gases should not mix at or near the wafer surface to prevent co-reaction (a co-reactive embodiment is disclosed elsewhere herein), and thus at least one gas purge or pump evacuation between precursor pulses should be used to prevent mixing.

Generally, a pulse time of less than about 1 second for a tantalum containing compound and a pulse time of less than about 1 second for a nitrogen containing

compound is typically sufficient to chemisorb alternating monolayers that comprise tantalum-nitride layer 204 on substrate 300. A pulse time of less than about 1 second for purge gas 138 is typically sufficient to remove reaction byproducts as well as any residual materials remaining in process chamber 100.

5 Sequential deposition as described advantageously provides good step coverage and conformality, due to using a chemisorption mechanism for forming tantalum-nitride layer 204. With complete or near complete saturation after each exposure of wafer 190 to a precursor, each of uniformity and step coverage is approximately 100 percent. Because atomic layer deposition is used, precision controlled thickness of tantalum-nitride layer
10 204 may be achieved down to a single layer of atoms. Furthermore, in ALD processes, since it is believed that only about one atomic layer may be absorbed on a topographic surface per "cycle," deposition area is largely independent of the amount of precursor gas remaining in a reaction chamber once a layer has been formed. By "cycle," it is meant a sequence of pulse gases, including precursor and purge gases, and optionally one or more pump evacuations. Also, by using ALD, gas-phase reactions between precursors is
15 minimized to reduce generation of unwanted particles.

Co-Reaction

Though it has been described to alternate tantalum and nitrogen containing
20 precursors and purging in between as applied in a sequential manner, another embodiment is to supply tantalum and nitrogen containing precursors simultaneously. Thus, pulses of gases 135 and 136, namely, tantalum and nitrogen containing compounds, are both applied to chamber 100 at the same time. An example is PEMAT and NH_3 , though other tantalum-organic and nitrogen precursors may be used. Step coverage and conformality is
25 good at approximately 95 to 100 percent for each. Moreover, deposition rate is approximately 0.001 to 0.1 microns per second. Because a co-reaction is used, purging between sequential pulses of alternating precursors is avoided, as is done in ALD.

Wafer surface temperature is maintained high enough to sustain reaction between two precursors. This temperature may be below chemisorption temperature of one or both
30 precursors. Accordingly, temperature should be high enough for sufficient diffusion of molecules or atoms.

Wafer surface temperature is maintained low enough to avoid significant decomposition of precursors. However, more decomposition of precursors may be acceptable for co-reaction than for sequentially reacting precursors in an ALD process. In general, wafer 190 surface diffusion rate of molecules or atoms should be greater than precursors' reaction rate which should be greater precursors' decomposition rate.

For all other details, the above-mentioned description for sequentially applied precursors applies to co-reaction processing.

Plasma Anneal

After forming one or more combinations of layers 305 and 307, substrate structure 250 may be plasma annealed. Referring to FIG. 4, there is illustratively shown a schematic diagram of an exemplary portion of a process system 10P in accordance with an aspect of the present invention. Process system 10P is similar to process system 10, except for additions of one or more RF power supplies 410 and 412, showerhead 400, gas source 405, and matching network(s) 411. Notably, a separate plasma process system may be used; however, by using a CVD/PVD process system 10P, less handling of substrate structure 250 is involved, as layer 204 may be formed and annealed in a same chamber 100.

Showerhead 400 and wafer support pedestal 150 provide in part spaced apart electrodes. An electric field may be generated between these electrodes to ignite a process gas introduced into chamber 100 to provide a plasma 415. In this embodiment, argon is introduced into chamber 100 from gas source 405 to provide an argon plasma. However, if argon is used as a purge gas, gas source 405 may be omitted for gas source 138.

Conventionally, pedestal 150 is coupled to a source of radio frequency (RF) power source 412 through a matching network 411, which in turn may be coupled to control unit 110. Alternatively, RF power source 410 may be coupled to showerhead 400 and matching network 411, which in turn may be coupled to control unit 110. Moreover, matching network 411 may comprise different circuits for RF power sources 410 and 412, and both RF power sources 410 and 412 may be coupled to showerhead 400 and pedestal 150, respectively.

With continuing reference to FIG. 4 and renewed reference to FIG. 3c, substrate structure 250 having one or more iterations or tantalum-nitride sublayers 309 is located in

process chamber 401. Argon (Ar) gas from gas source 405 is introduced into chamber 401 to plasma anneal substrate structure 250. While not wishing to be bound by theory, it is believed that plasma annealing reduces nitrogen content of one or more sublayers 309 by sputtering off nitrogen, which in turn reduces resistivity. In other words, plasma annealing is believed to make tantalum-nitride layer 204 more tantalum-rich as compared to a non-plasma annealed tantalum-nitride layer 204. For example, a 1:1 Ta:N film may be annealed to a 2:1 Ta:N film. Tantalum-nitride films having a sheet resistance of approximately equal to or less than 1200 micro-ohms-cm for 0.004 micron (40 Angstrom) films may be achieved.

It will be appreciated that other non-chemically reactive gases with respect to layer 204 may be used for physically displacing nitrogen from layer 204, including but not limited to neon (Ne), xenon (Xe), helium (He), and hydrogen (H₂). Generally, for a plasma-gas that does not chemically react with a tantalum-nitride film, it is desirable to have a plasma-gas atom or molecule with an atomic-mass closer to N than to Ta in order to have preferential sputtering of the N. However, a chemically reactive process may be used where a gas is selected which preferentially reacts for removal of N while leaving Ta.

Referring to FIG. 5, there is illustratively shown a cross sectional view of layer 204 after plasma annealing in accordance with a portion of an exemplary embodiment of the present invention. Plasma annealing may be done after formation of each nitrogen layer 307, or may be done after formation of a plurality of layers 307. With respect to the latter, plasma annealing may take place after approximately every 0.003 to 0.005 microns (30 to 50 Angstroms) of layer 204 or after formation of approximately every 7 to 10 sublayers 309. However, plasma annealing may be done after formation of a sublayer 309, which is approximately 0.0001 to 0.0004 microns (1 to 4 Angstroms).

Plasma annealing with argon may be done with a wafer temperature in a range of approximately 20 to 450 degrees Celsius and a chamber pressure of approximately 0.1 to 50 Torr with a flow rate of argon in a range of approximately 10 to 2000 standard cubic centimeters per minute (sccm) with a plasma treatment time approximately equal to or greater than one second. Generally, a tantalum-nitride film should be annealed at a temperature, which does not melt, sublime, or decompose such a tantalum-nitride film.

The specific process conditions disclosed in the above description are meant for illustrative purposes only. Other combinations of process parameters such as precursor

2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023 2024 2025 2026 2027 2028 2029 2030 2031 2032 2033 2034 2035 2036 2037 2038 2039 2040 2041 2042 2043 2044 2045 2046 2047 2048 2049 2050 2051 2052 2053 2054 2055 2056 2057 2058 2059 2060 2061 2062 2063 2064 2065 2066 2067 2068 2069 2070 2071 2072 2073 2074 2075 2076 2077 2078 2079 2080 2081 2082 2083 2084 2085 2086 2087 2088 2089 2090 2091 2092 2093 2094 2095 2096 2097 2098 2099 2100 2101 2102 2103 2104 2105 2106 2107 2108 2109 2110 2111 2112 2113 2114 2115 2116 2117 2118 2119 2120 2121 2122 2123 2124 2125 2126 2127 2128 2129 2130 2131 2132 2133 2134 2135 2136 2137 2138 2139 2140 2141 2142 2143 2144 2145 2146 2147 2148 2149 2150 2151 2152 2153 2154 2155 2156 2157 2158 2159 2160 2161 2162 2163 2164 2165 2166 2167 2168 2169 2170 2171 2172 2173 2174 2175 2176 2177 2178 2179 2180 2181 2182 2183 2184 2185 2186 2187 2188 2189 2190 2191 2192 2193 2194 2195 2196 2197 2198 2199 2200 2201 2202 2203 2204 2205 2206 2207 2208 2209 2210 2211 2212 2213 2214 2215 2216 2217 2218 2219 2220 2221 2222 2223 2224 2225 2226 2227 2228 2229 2230 2231 2232 2233 2234 2235 2236 2237 2238 2239 2240 2241 2242 2243 2244 2245 2246 2247 2248 2249 2250 2251 2252 2253 2254 2255 2256 2257 2258 2259 2260 2261 2262 2263 2264 2265 2266 2267 2268 2269 2270 2271 2272 2273 2274 2275 2276 2277 2278 2279 2280 2281 2282 2283 2284 2285 2286 2287 2288 2289 2290 2291 2292 2293 2294 2295 2296 2297 2298 2299 2300 2301 2302 2303 2304 2305 2306 2307 2308 2309 2310 2311 2312 2313 2314 2315 2316 2317 2318 2319 2320 2321 2322 2323 2324 2325 2326 2327 2328 2329 2330 2331 2332 2333 2334 2335 2336 2337 2338 2339 2340 2341 2342 2343 2344 2345 2346 2347 2348 2349 2350 2351 2352 2353 2354 2355 2356 2357 2358 2359 2360 2361 2362 2363 2364 2365 2366 2367 2368 2369 2370 2371 2372 2373 2374 2375 2376 2377 2378 2379 2380 2381 2382 2383 2384 2385 2386 2387 2388 2389 2390 2391 2392 2393 2394 2395 2396 2397 2398 2399 2400 2401 2402 2403 2404 2405 2406 2407 2408 2409 2410 2411 2412 2413 2414 2415 2416 2417 2418 2419 2420 2421 2422 2423 2424 2425 2426 2427 2428 2429 2430 2431 2432 2433 2434 2435 2436 2437 2438 2439 2440 2441 2442 2443 2444 2445 2446 2447 2448 2449 2450 2451 2452 2453 2454 2455 2456 2457 2458 2459 2460 2461 2462 2463 2464 2465 2466 2467 2468 2469 2470 2471 2472 2473 2474 2475 2476 2477 2478 2479 2480 2481 2482 2483 2484 2485 2486 2487 2488 2489 2490 2491 2492 2493 2494 2495 2496 2497 2498 2499 2500 2501 2502 2503 2504 2505 2506 2507 2508 2509 2510 2511 2512 2513 2514 2515 2516 2517 2518 2519 2520 2521 2522 2523 2524 2525 2526 2527 2528 2529 2530 2531 2532 2533 2534 2535 2536 2537 2538 2539 2540 2541 2542 2543 2544 2545 2546 2547 2548 2549 2550 2551 2552 2553 2554 2555 2556 2557 2558 2559 2560 2561 2562 2563 2564 2565 2566 2567 2568 2569 2570 2571 2572 2573 2574 2575 2576 2577 2578 2579 2580 2581 2582 2583 2584 2585 2586 2587 2588 2589 2590 2591 2592 2593 2594 2595 2596 2597 2598 2599 2600 2601 2602 2603 2604 2605 2606 2607 2608 2609 2610 2611 2612 2613 2614 2615 2616 2617 2618 2619 2620 2621 2622 2623 2624 2625 2626 2627 2628 2629 2630 2631 2632 2633 2634 2635 2636 2637 2638 2639 2640 2641 2642 2643 2644 2645 2646 2647 2648 2649 2650 2651 2652 2653 2654 2655 2656 2657 2658 2659 2660 2661 2662 2663 2664 2665 2666 2667 2668 2669 2670 2671 2672 2673 2674 2675 2676 2677 2678 2679 2680 2681 2682 2683 2684 2685 2686 2687 2688 2689 2690 2691 2692 2693 2694 2695 2696 2697 2698 2699 2700 2701 2702 2703 2704 2705 2706 2707 2708 2709 2710 2711 2712 2713 2714 2715 2716 2717 2718 2719 2720 2721 2722 2723 2724 2725 2726 2727 2728 2729 2730 2731 2732 2733 2734 2735 2736 2737 2738 2739 2740 2741 2742 2743 2744 2745 2746 2747 2748 2749 2750 2751 2752 2753 2754 2755 2756 2757 2758 2759 2760 2761 2762 2763 2764 2765 2766 2767 2768 2769 2770 2771 2772 2773 2774 2775 2776 2777 2778 2779 2780 2781 2782 2783 2784 2785 2786 2787 2788 2789 2790 2791 2792 2793 2794 2795 2796 2797 2798 2799 2800 2801 2802 2803 2804 2805 2806 2807 2808 2809 2810 2811 2812 2813 2814 2815 2816 2817 2

Although several preferred embodiments, which incorporate the teachings of the present invention, have been shown and described in detail, those skilled in the art can readily devise many other varied embodiments that still incorporate these teachings. By way of example and not limitation, it will be apparent to those skilled in the art that the above-described formation is directed at atomic layer CVD (ALCVD); however, low temperature CVD may be used as described with respect to co-reacting precursors. Accordingly, layers 305 and 307 need not be monolayers. Moreover, it will be appreciated that the above described embodiments of the present invention will be particularly useful in forming one or more barrier layers for interconnects on semiconductor devices having a wide range of applications.